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(21) International Application Number: PCT/US96/18507 (22) International Filing Date: 18 November 1996 (18.11.96) (30) Priority Data: 08/559,006 16 November 1995 (16.11.95) US (71) Applicant: H.B. FULLER LICENSING & FINANCING, INC. [US/US]; 1200 Willow Lake Boulevard, St. Paul, MN 55110-5132 (US). (72) Inventors: SIMMONS, Eugene; 3440 Montmorency Street, Vadnais Heights, MN 55110 (US). SWEENEY, Kevin; 338 Wedgewood Drive, Mahtomedi, MN 55115 (US). LINDQUIST, Jeffrey; 9646 Indian Boulevard, Cottage Grove, MN 55016 (US). OLSON, Christopher; 5154 Parkside Drive, Paducah, KY 42001 (US). CARTES, Freddie; 1020 Wayside Drive, Paducah, KY 42003 (US). FARMER, James; 602 Newton, Johnston, IL 62951 (US). (74) Agents: STEINKRAUS, Walter, J. et al.; 1540 Kinnard Financial Center, 920 Second Avenue South, Minneapolis, MN 55402 (US).		(81) Designated States: AU, BR, CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: A POLYMERIC COMPOSITION IN PELLET FORM (57) Abstract A polymeric composition in pellet form comprising a tacky hot melt composition, comprising a) from about 5 % by weight to about 90 % by weight of a thermoplastic polymer, b) from about 10 % by weight to about 65 % by weight of a tackifying resin, c) up to about 50 % by weight of a plasticizer, d) up to about 2 % by weight of an antioxidant, and a pelletizing aid, wherein the tacky hot melt composition is a pressure sensitive adhesive having a storage modulus, G', at about 25 °C, of less than about 5 x 10 ⁶ dynes/cm ² , and each pellet has a substantially tack-free surface. This invention further discloses a polymeric composition in pellet form suitable for molding articles. The composition comprises a tacky hot melt composition comprising at least one high molecular weight triblock copolymer of the general configuration A-B-A and a plasticizer and a pelletizing aid. The pelletizing aid substantially surrounds the tacky composition such that the molded articles are substantially free from surface tack. A method of forming the pellets is also disclosed.		

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A POLYMERIC COMPOSITION IN PELLET FORM

Field Of The Invention

This invention relates to a polymeric composition in pellet form comprising a tacky hot melt composition which can be used either for hot melt pressure sensitive applications or for molded articles. Those compositions suitable for pressure sensitive applications are defined by having a storage modulus, G' , at 25°C, of less than about 5×10^6 dynes/cm², and each pellet has a substantially tack-free surface prior to melting, and pressure sensitive characteristics after resolidification. The polymeric compositions suitable for use in injection molding preferably comprise a high molecular weight block copolymer and have a tack-free surface both prior to melting the pellets, and after melting and resolidification.

Background Of The Invention

Tacky hot melt compositions have been used widely in the adhesive industry for a wide range of applications such as for pressure sensitive adhesives due to their ability to adhere to a wide variety of substrates. A primary property of a hot melt pressure sensitive composition is that it remain tacky at room temperature so that it may be adhered to substrates when it has completely cooled from its molten state. Examples of applications which require this property are tape and label applications. Paper, polyethylene, polypropylene or other such substrates may be coated with the tacky hot melt composition, covered with release liner, and then shipped this way for later applications such as for labels used on various containers, books, magazines, or envelopes just to name a few.

The use of tacky hot melt compositions in other applications has been precluded by the fact that they remain tacky. Yet it may be desirable to use these soft and very flexible compositions for other applications. One such application

is the formation of articles by injection molding. Some articles formed by injection molding include shoe soles, drum pads, therapeutic hand exercising grips, shock absorbers, acoustical insulators, chair pads and imitation skin for use in the entertainment industry but this list is not exhaustive.

5 The tackiness exhibited by these hot melt pressure sensitive adhesives also makes them difficult to handle. They may adhere to skin, clothing, application equipment, floors, or other places that are undesirable. Many packaging methods have been devised to avoid the problems encountered in the handling of these hot melt pressure sensitive compositions.

10 Hot melt adhesives are supplied as pellets, pillows as disclosed by German Pat. 22 48 046, slats or chicklets, blocks, and cakes.

A further problem encountered with hot melt pressure sensitive adhesives is that the tackiness may result in blocking individual pieces together resulting in a large mass in the shipping containers. This makes it difficult to get the adhesive
15 into many different types of hot melt premelter tanks used in the industry.

U.S. Pat. No. 3,723,035 discloses a machine performing an improved method of packaging a hot melt adhesive. This produces an end product known as pillows to one of skill in the art. These pillows can be coextruded with a non-tacky polymer such as polyethylene for producing pressure sensitive adhesives
20 that are tacky at room temperature. This coextrusion coating prevents the pillows from blocking together in a solid mass at room temperature. Using this method, once the coextruded pillows are melted for use on an application line, the hot melt composition again becomes tacky when it returns to room temperature.

French Pat. No. 2,544,654 published Oct. 26, 1984 discloses forming a
25 tackless hot melt by adding the molten hot melt to a mold which contains a preformed support layer having a transfer film which is compatible with the hot melt.

U.S. Pat. No. issued June 12, 1988 and 4,755,245 issued July 5, 1988 disclose forming a protective coating for an adhesive material by electrostatically
30 coating a mold or cavity with a powder screen and then pouring hot melt into the mold.

French Pat. No. 2,601,616 published Oct. 22, 1988 discloses forming blocks of hot melt pressure sensitive adhesive by casting the adhesive into molds precoated by spraying with a film of non self-sticking hot melt material.

German Pat. Nos. DE 31 38 222, DE 32 34 065, and DE 36 25 358 teach
5 coating or wrapping a formed hot melt block with various types of film.

U.S. Pat. No. 5,257,491 to Rouyer et al. teaches a method of packaging a hot melt adhesive composition wherein the adhesive composition is sufficiently solidified or when flowable.

U.S. Pat. No. 5,401,455 to Hatfield et al. issued March 28, 1995 teaches a
10 method for packaging hot melt adhesive compositions comprising the use of a mold being in contact with a refrigerant gas or liquid heat sink. Hatfield teaches that when a hot melt adhesive is poured into a cavity lined with film in its molten state, the adhesive is fused to some extent with the film. According to Hatfield, this in turn allows some mixing and compatibilizing of the film, improving the
15 opportunity for more complete mixing.

U.S. Pat. No. 5,057,571 to Malcolm et al. discloses at column 8 line 59 to column 9 line 14 a method for pelletizing a preblend of a radial block copolymer and a tackifying resin. This preblend is then used to make hot melt adhesives for disposable article construction. The preblend is manufactured on an extruder.
20 The pelletized preblend was then used to make an adhesive using conventional hot melt mixers. This is a two step process of making hot melt pressure sensitive adhesives, and it was never intended to teach making a finished product in a free-flowing pellet form.

The current inventors have found a polymeric composition in a free-
25 flowing pellet form that can be either a hot melt pressure sensitive adhesive or a polymeric composition that has a surface that remains tack-free after melting and resolidification.

Summary Of The Invention

The present invention discloses a polymeric composition in pellet form, comprising:

- I. from about 97 to about 99.9 percent by weight of a tacky hot melt composition, comprising:
 - a) from about 5% to about 90% by weight of a thermoplastic polymer;
 - b) from about 0% to about 65% of a tackifying resin;
 - c) from about 0% to about 50% by weight of a plasticizer; and
 - d) up to about 2% of an antioxidant; and
- II. from about 0.1% to about 3% by weight of a pelletizing aid, wherein the composition comprises some minimum amount of tackifier or plasticizer or both.

The tacky hot melt composition is a pressure sensitive adhesive having a storage modulus, G' , at 25°C, of less than about 5×10^6 dynes/cm², as measured using a Rheometrics Scientific Dynamic Mechanical Spectrometer Model #RDS7700.

The pelletizing aid is used to provide hot melt pressure sensitive adhesives in pellet form wherein the pellet has a tack-free surface. Once the pellets are melted and resolidified, these compositions once again return to their original tacky state. These pellets are free-flowing and the resultant pelletized composition can be used in various tape and label applications, in non-woven applications where pressure sensitive adhesives are used such as for positioning of feminine napkins, diaper fastening systems, and disposable article construction, in the automotive industry where hot melt pressure sensitive adhesives are used for assembly applications, and for medical applications.

The present invention further discloses a polymeric composition in pellet form, comprising:

- I. from about 97 to about 99.9 percent by weight of a tacky hot melt composition, comprising:

- a) from about 2.0 to about 20 percent by weight of a block copolymer having the general configuration A-B-A and a molecular weight greater than about 200,000;
- b) from about 20 to about 98 percent by weight of a compatible plasticizer; and
- c) from about 0% to about 30 percent by weight of a compatible block copolymer;

II. from about 0.1% to about 3 percent by weight of a pelletizing aid.

The resultant polymeric compositions have a tack-free surface both prior to melting the pellets, and after melting and resolidification.

The resultant tacky hot melt compositions are characterized by a specific gravity of greater than about 0.8, Mettler Softening Points of greater than about 90°C and Bloom Gelometer readings of greater than about 20 grams.

The pellets thus formed are soft, non-blocking, substantially without surface tack and exhibit an elastic rebound, as characterized by G' (elastic or storage modulus) measurements. These compositions are suitable for use in molding, especially injection molding. Any molded products produced therefrom also retain the substantially tack-free surface. While the bulk composition determines the properties of the pellets, the pelletizing aid determine the surface properties of the pellets, and has no effect on the bulk properties.

These pellets are suitable for use in molding, especially injection molding.

The composition suitable for such processes comprises:

I. A tacky hot melt composition, comprising:

- a) at least one high molecular weight triblock copolymer of the general configuration A-B-A; and
- b) a plasticizer; and

II. A pelletizing aid,

wherein said pelletizing aid substantially surrounds the tacky composition such that the molded articles are soft, non-blocking and have a substantially tack-free surface. Optionally, other compatible block copolymers such as radial blocks and diblocks and other triblocks can be added. Preferably, the tacky hot melt

composition comprises from about 97 to about 99.9 percent by weight of the article, more preferably from about 99 to about 99.9 percent by weight.

Any molded articles produced therefrom also retain the substantially tack-free surface and rebound properties. Such articles can include drum pads useful as
5 acoustical pads for vibration damping, disc players, ear phones, percussion surfaces on electronic drum kits and so on; soles, shoes insoles, in-line skate soles and so on; pads for use in athletic gear such as mouth pads, protective guards, encapsulants for other solid protective pads and so on; bicycle seats, gloves, bicycle shorts and so on; medical equipment such as pads for wheel chairs, donut-
10 shaped pads for seats and so on; furniture pads such as mattress pads, chair pads and so on; special effects articles such as body parts, Santa Claus' bellies, synthetic skin, and others that are useful in movies; and bandages, especially for burn wounds. While the rest of the composition determines the overall bulk properties of the pellets and articles molded therefrom, the pelletizing aid
15 determines the surface properties of not only the pellets, but the articles made from such pellets.

The present invention also discloses an under-water pelletizing process for making the tacky hot melt compositions in pellet form, utilizing a pelletizing aid to produce pellets that have a substantially tack-free surface making them non-
20 blocking, and are soft. The process varies slightly for each product, dependent mainly on the plasticizer loading, and comprises the steps of:

- a) blending the hot melt components to form a substantially homogeneous hot melt mixture;
- b) forcing said substantially homogeneous hot melt mixture through a
25 die for forming substantially homogeneous hot melt ribbons and forming resultant pellets therefrom;
- c) solidifying said pellets by use of a cooling medium; and
- d) applying said pelletizing aid at some point during the pelletizing process.

30 The pellets can be made into any convenient size. Preferably, the pellets are substantially spherical, with sizes ranging from about 1/8 to about 3/8 inch (about 3mm to about 10mm) in diameter for easy handling. The pellets can also

be ellipsoidal and cylindrical. The preferred dimensions for these shapes can range from about 3mm to about 10mm to about 10mm by 20mm.

Detailed Descriptions Of The Preferred Embodiments

- 5 The pelletized polymeric compositions of the present invention can exhibit a spectrum of properties, ranging from compositions having hot melt pressure sensitive adhesive properties to compositions suitable for molding non-tacky articles. Those polymeric compositions for use in pressure sensitive applications have a storage modulus, G' , at 25°C of less than about 5×10^6 dynes/cm², and
- 10 preferably have a storage modulus, G' , at about 25°C, from about 1×10^4 to about 5×10^6 dynes/cm² while those useful for molding applications can have a storage modulus of greater than about 5×10^6 dynes/cm². The storage modulus, G' , is measured using a Rheometrics Scientific Dynamic Mechanical Spectrometer Model #RDS7700.
- 15 The thermoplastic polymers useful for the present invention can include A-B-A triblock copolymers, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers, radial block copolymers and grafted versions thereof; homopolymers, copolymers and terpolymers of ethylene; and homopolymers, copolymers and terpolymers of propylene; and mixtures thereof. Radial block copolymers include
- 20 Y-block and star polymers as well as other configurations. The A-B-A block copolymers useful herein are those described in U.S. Pat. No. 4,136,699 to (Collins et al.), incorporated herein by reference, issued January 30, 1979. Examples include those polymers available under the Kraton™ G series from Shell Chemical Co. in Houston, TX. There are various grades available including
- 25 Kraton™ G-1726, Kraton™ G-1650, Kraton™ G-1651, Kraton™ G-1652, Kraton™ G-1657, all saturated A-B diblock/A-B-A triblock mixtures with ethylene/butylene midblocks; Kraton™ D-1112 a high percent A-B diblock linear styrene-isoprene-styrene polymer; Kraton™ D-1107 and Kraton™ D-1111, primarily A-B-A triblock linear styrene-isoprene-styrene block copolymers;
- 30 Kraton D4433X, a linear SIS block copolymer with an oil content of 30% by weight and Kraton D1184, a high molecular weight SBS block copolymer both available from Shell Chemical Co.: Stereon™ 840A and Stereon™ 841A. A-B-A-

B-A-B multiblock SBS block copolymers available from Firestone in Akron, Ohio; Europrene™ Sol T-193B, a linear SIS block copolymer available from Enichem Elastomers in New York, NY; Europrene™ Sol T-190, a linear styrene-isoprene-styrene block copolymer and Europrene™ Sol T-163, a radial SBS block copolymer both also available from Enichem Elastomers; Vector™ 4461-D, a linear SBS block copolymer available from Exxon Chemical Co. in Houston, Texas; Vector™ 4111, 4211 and 4411, fully coupled linear SIS block copolymers containing different weight percentages of styrene endblock; and Vector™ 4113, a highly coupled linear SIS block copolymer also available from Exxon Chemical Co.; and DPX-550, DPX-551 and DPX-552 radial SIS block copolymers available from Dexco Polymers in Houston, Texas. This list is not exclusive and there are numerous grades of block copolymers available from various sources for hot melt pressure sensitive adhesives. These polymers may be used alone, or in any combinations. These polymers are useful from about 5% to about 90% by weight in the polymeric composition.

The polymeric compositions suitable for molding applications may comprise any of the above mentioned polymers which have a high molecular weight and preferably have a weight average molecular weight greater than about 200,000 as measured by Gel Permeation Chromatography, with values reported relative to styrene standards. The polymer is preferably a substantially linear copolymer having the general configuration A-B-A, wherein the A block can be polystyrene and the B block can be ethylene-butylene, ethylene-propylene, isoprene, butadiene or mixtures thereof, and preferably the B block is ethylene-butylene or ethylene-propylene. Polymers of this type, such as Kraton™ G-1651, are twice the molecular weight of conventional styrene-ethylene/butylene-styrene (S-EB-S) block copolymers used in the hot melt adhesive industry. This copolymer is present in amounts from about 2 to about 20 percent by weight and preferably from about 5 to about 20 percent by weight in the polymeric composition.

Other lower molecular weight block copolymers may be utilized with these high molecular weight block copolymers. Some examples are A-B-A triblock copolymers, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers,

radial block copolymers, and grafted versions of such copolymers including Shell Chemical's TKG-101 and RP-6912. Such A-B-A block copolymers are disclosed in Collins et al., U.S. Pat. No. 4,136,699. Some of these block copolymers are commercially available from Shell Chemical Co. under the Kraton™ G series
5 which are S-EB-S block copolymers.

Other useful polymers include atactic polyalphaolefins such as those available from Rexene Products Co. in Dallas, Texas under the tradename of Rextac™ such as RT-2280 and RT-2315 and RT-2585 having various amounts of ethylene and homogeneous linear or substantially linear interpolymers of ethylene
10 with at least one C₂ to C₂₀ alphaolefin, further characterized by each said interpolymers having a polydispersity less than about 2.5 including such polymers as Exact™ 5008, an ethylene-butene copolymer, Exxpol SLP-0394™, and ethylene-propylene copolymer, Exact™ 3031, an ethylene-hexene copolymer, all available from Dow Chemical Co. in Midland, MI. These polymers may have to
15 be used in small concentrations if utilized with such block copolymers as Kraton™ G-1651 to maintain compatibility without phase separation or snotty, gel-like compositions. These concentrations may be as low as 5% by weight in the composition.

Other compatible polymers may be useful in the polymeric compositions
20 of the present invention including ethylene vinyl acetate copolymers such as Elvax™ 410, a 14% vinyl acetate/400 melt index copolymer and Elvax™ 210, a 28% vinyl acetate/400 melt index copolymer, both available from DuPont Chemical Co. in Wilmington, DE; Escorene™ UL 7505 an ethylene vinyl acetate copolymer available from Exxon Chemical Co.; Ultrathene™ UE 64904 available
25 from Quantum Chemical Co., U.S.I. Division in Cincinnati, OH; and AT 1850M available from AT Polymers & Film Co. in Charlotte, North Carolina. Copolymers of ethylene and methyl acrylate (methacrylates as well as acrylates) are also useful including Optema™ TC-140, XS-93.04 and TC-221 available from Exxon Chemical Co.; Lotryl™ 28 MA 175 and 35 MA 05 1000 available from Elf
30 Atochem North America in Philadelphia, PA. Ethylene methyl acrylate copolymers are also available from Chevron under the tradename of Emac™ and from Quantum Chemical Co. under the tradename of Acrythene™. Copolymers

of ethylene and n-butyl acrylate are also useful in the adhesives of the invention. They are available from Quantum Chemical Co. under the tradename of Enathene™ including EA80808, EA 89821 and EA89822; from Elf Atochem North America under the tradename of Lotryl™ including 35 BA 900 and 35 BA 1000; from Exxon Chemical Co. under the tradename of Escorene™ including XW-23.AH and XW-22. These polymers may also have to be used in small concentrations with some of the block copolymers such as Kraton™ G-1651.

The polymeric compositions may also comprise a tackifying resin. While they are preferable for use in hot melt pressure sensitive compositions, they may or may not be utilized in the molded article compositions. The tackifying resins useful herein include aliphatic, cycloaliphatic and aromatic hydrocarbons and modified hydrocarbons and hydrogenated derivatives; terpenes and modified terpenes and hydrogenated derivatives; rosins and modified rosins and hydrogenated derivatives; and mixtures thereof. These tackifying resins have a ring and ball softening point of between about 70°C and 150°C. They are also available with differing levels of hydrogenation, or saturation which is another commonly used term. Useful examples include Eastotac™ H-100, H-115 and H-130 from Eastman Chemical Co. in Kingsport, TN which are partially hydrogenated cycloaliphatic petroleum hydrocarbon resins with different softening points. These are available in the E grade, the R grade, the L grade and the W grade. These have differing levels of hydrogenation from least hydrogenated to most hydrogenated. The E grade has a bromine number of 15, the R grade a bromine number of 5, the L grade has a bromine number of 3 and the W grade a bromine number of 1. There is also an Eastotac™ H-142R resin available. Other useful tackifying resins include Escorez 1310 LC, an aliphatic hydrocarbon resin, Escorez™ 5300 and Escorez™ 5400, partially hydrogenated cycloaliphatic petroleum hydrocarbon resins, and Escorez™ 5600, a partially hydrogenated aromatic modified petroleum hydrocarbon resin all available from Exxon Chemical Co. in Houston, TX; Wingtack™ Extra which is an aliphatic, aromatic petroleum hydrocarbon resin available from Goodyear Chemical Co. in Akron, OH; Herculite™ 2100 which is a partially hydrogenated cycloaliphatic petroleum hydrocarbon resin available from Hercules in Wilmington, DE; and

Zonatac™ 105 Lite which is a styrenated terpene resin made from d-limonene and available from Arizona Chemical Co. in Panama City, FL. There are numerous types of rosins and modified rosins available with differing levels of hydrogenation including gum rosins, wood rosins, tall-oil rosins, distilled rosins, dimerized rosins and polymerized rosins. Some specific modified rosins include glycerol and pentaerythritol esters of wood rosins and tall-oil rosins. Commercially available grades include, but are not limited to, Sylvatac™ 1103, a pentaerythritol rosin ester available from Arizona Chemical Co., Unitac™ R-100 Lite a pentaerythritol rosin ester from Union Camp in Wayne, NJ, Zonester™ 100, a glycerol ester of tall oil rosin from Arizona Chemical Co., Permalyn™ 305, a pentaerythritol modified wood rosin available from Hercules, Inc. in Wilmington, DE and Foral™ 105, which is a highly hydrogenated pentaerythritol rosin ester available. Sylvatac™ R-85 which is an 85°C melt point rosin acid and Sylvatac™ 295 which is a 95°C melt point rosin acid are both available from Arizona Chemical Co.. Foral™ AX is a 75°C melt point hydrogenated rosin acid available from Hercules Inc. Nirez™ V-2040 is a phenolic modified terpene resin available from Arizona Chemical Co. There are many available types and grades of tackifying resins available from many companies, and one skilled in the art would recognize that this is not an exclusive list, and that the available tackifying resins are too numerous to list here. Various endblock resins are also useful in the compositions of the present invention. These include Endex™ 160, an aromatic hydrocarbon manufactured by Hercules, Inc. in Wilmington, DE; Kristalex™ 3100 and Kristalex™ 5140, alphas-methyl styrene hydrocarbons manufactured by Hercules, Inc.; and also coumarone indene resins. These tackifiers are useful from about 0% to about 65% by weight, and preferably from about 10% to about 65%.

The plasticizers useful in the present invention may include mineral based oils and petroleum based oils, liquid resins, liquid elastomers, polybutene, polyisobutylene, functionalized oils such as glycerol trihydroxyoleate and other fatty oils and mixtures thereof. A plasticizer is broadly defined as a typically organic composition that can be added to the thermoplastics, rubbers and other resins to improve extrudability, flexibility, workability and stretchability in the

finished adhesive. Any material which flows at ambient temperatures and is compatible with the block copolymer may be useful.

The most commonly used plasticizers are oils which are primarily hydrocarbon oils that are low in aromatic content and are paraffinic or naphthenic in character. The oils are preferably low in volatility, transparent and have as little color and odor as possible. This invention also contemplates the use of olefin oligomers, low molecular weight polymers, vegetable oils and their derivatives and similar plasticizing oils.

Examples of useful plasticizers include Calsol™ 5120, a naphthenic petroleum based oil available from Calumet Lubricants Co. in Indianapolis, IN; Kaydol™ White Mineral Oil, a paraffinic mineral oil available from Witco Corp. in New York, NY; Parapol™ 1300, a liquid butene homopolymer available from Exxon Chemical Co. in Houston, TX; Indopol™ H-300, a liquid butene homopolymer, available from Amoco Corp. in Chicago, IL; Escorez™ 2520, a liquid aromatic petroleum based hydrocarbon resin with a pour point of 20°C, available from Exxon Chemical Co.; Regalrez™ 1018, a liquid hydrogenated aromatic hydrocarbon resin with a pour point of 18°C, available from Hercules, Inc. in Chicago, IL; and Sylvatac™ 5N, a liquid resin of modified rosin ester with a pour point of 5°C, available from Arizona Chemical Co. in Panama City, FL.

One skilled in the art would recognize that any generic 500 second or 1200 second naphthenic process oil would also be useful. These plasticizers are useful in amounts from about 0% to about 50% by weight for the hot melt pressure sensitive compositions, and up to about 98% by weight in the molded article compositions, and preferably up to about 90% by weight.

A pelletizing aid is used to change the surface characteristics of the pellets. It would be generally undesirable for molded articles manufactured by such methods as injection molding, to remain tacky. Surprisingly, a small amount of pelletizing aid can make the surface of the pellets substantially non-tacky. The pelletizing aids do not change the end use properties of the tacky composition, as in the formulas used as hot melt pressure sensitive adhesives, or they do change the physical properties of the tacky composition, as in the case of the formulas used for the molding applications.

The pelletizing aid is selected from the group consisting of polyethylene waxes, modified polyethylene waxes, polyamide waxes and stearamide waxes. Many other waxes or pelletizing aids not on this list could also be useful provided the surface of the resultant pellet is tack-free. Preferred waxes are Acrawax C™
5 stearamide wax available from Lonza, Inc. in Fairlawn, NJ; Castor™ hydroxy waxes and Paricin™ hydroxyamide waxes available from Caschem in Bayonne, NJ; Neptune™ 968 available from Shamrock Technologies in Newark, NJ; Shamrock™ S-395 polyethylene wax available from Shamrock Technologies; and Hoechst™ Wax PED 121, a modified polyethylene available from Hoechst
10 Celanese in Somerville, NJ. More preferably, these pelletizing aids are polyethylene waxes and come in powder form. The pelletizing aid is present from about 0.1 percent to about 3 percent by weight and preferably from about 0.1 percent to about 1 percent by weight. This amount is substantially less or comparable to the packaging film of prior art packaging methods. It is believed
15 that the temperature of use of the tacky hot melt composition controls whether the surface of tacky hot melt composition returns to the substantially tack-free state after melting the pellets, and subsequent resolidification.

A stabilizer or antioxidant can also be used in the polymeric compositions. These compounds are added to protect the adhesive from degradation caused by
20 reaction with oxygen induced by such things as heat, light or residual catalyst from the raw materials such as the tackifying resin. Such antioxidants are commercially available from Ciba-Geigy in Hawthorne, NY and include Irganox™ 565, Irganox™ 1010 and Irganox™ 1076, all hindered phenolic antioxidants. These are primary antioxidants which act as free radical scavengers
25 and may be used alone or in combination with other antioxidants such as phosphite antioxidants like Irgafos™ 168 available from Ciba-Geigy. Phosphite antioxidants are considered secondary antioxidants, are primarily used as peroxide decomposers and are generally not used alone, but are instead used in combination with other antioxidants. Other available antioxidants are Cyanox™ LTDP, a
30 thioether antioxidant, available from Cytec Industries in Stamford, CT, Ethanox™ 330, a hindered phenolic antioxidant, available from Albemarle in Baton Rouge, LA. Many other antioxidants are available for use by themselves, or in

combination with other antioxidants. These compounds are added to the hot melts in small amounts, up to about 2% by weight in the hot melt pressure sensitive adhesive, and have no effect on the physical properties of the adhesive.

Other compounds that also could be added that have no effect on the physical properties are pigments which add color, fluorescing agents, any compounds that mask odor and fillers to mention only a few. Additives such as these are known to one of skill in the art.

Fillers come in the form of particulate matter, fibers and powders, or may be any material that does not interfere with the other components in the adhesive. Some examples include calcium carbonate, ceramics, glass, silica, quartz, mica, treated clay, titanium dioxide, boron nitrides, graphite, carbon black, metals, barium, sulfate, talc and mixtures thereof. Such additives are known to one of skill in the art.

As discussed above, the resultant pellets are soft, non-blocking, substantially free from surface tack and exhibit an elastic rebound. This last characteristic can be measured by the elastic or storage modulus, G' . The higher the modulus, the more likely that the material will return to its original shape. At lower loadings of the high molecular weight triblock copolymer, the pellets formed resemble gels. They possess some elastic rebound, but tend to retain the same physical property over a wide-temperature range, or over a long period of time. These pellets are desirable for making articles such as Santa Claus' bellies. At higher loadings of the copolymer, the pellets formed have high elastic modulus and tend to return to their original shape faster. They are more suited for producing articles such as drum pads.

Compatible polymers or copolymers discussed above can also be added to modify the properties of the pellets. These are generally of low molecular weight, and pellets made with an amount of the high molecular weight triblock copolymer tend to have more rebound than those made with the same amount of a blend of this copolymer and the low molecular weight compatible polymer or copolymer. These compatible polymers or copolymers are thus added for customizing the final applications or uses.

These pellets are suitable for use in molding, especially injection molding.
The composition suitable for such processes comprises:

- I. A tacky hot melt composition, comprising:
 - a) at least one high molecular weight triblock copolymer of
5 the general configuration A-B-A; and
 - b) a plasticizer; and
- II. A pelletizing aid;

wherein said pelletizing aid substantially surrounds the tacky composition such that the molded articles are soft, non-blocking and substantially without surface
10 tack. Optionally, other polymers such as diblock or other triblocks can be added. Preferably, the tacky hot melt composition comprises from about 97 to about 99.9 percent by weight of the article, more preferably from about 99 to about 99.9 percent by weight.

Any molded articles produced therefrom also retain the substantially tack-
15 free surface and rebound properties. Such articles can include drum pads useful as acoustical pads for vibration damping, disc players, ear phones, percussion surfaces on electronic drum kits and so on; soles shoes insoles, in-line skate soles and so on; pads for use in athletic gear such as mouth pads, protective guards, encapsulants for other solid protective pads and so on; bicycle seats, gloves,
20 bicycle shorts and so on; medical equipment such as pads for wheel chairs, donut-shaped pads for seats and so on; furniture pads such as mattress pads, chair pads and so on; special effects articles such as body parts, Santa Claus' bellies, and other that are useful in movies. Unlike the prior art, the pelletizing aid used herein blooms to the surface during the molding process, such that it substantially
25 completely surrounds the tacky composition below and produces articles substantially free of surface tack when cooled. This is surprising because the amount of pelletizing aid used in the formulation is small, and according to prior art teachings, should not substantially interfere with the properties of the bulk composition, nor should it change the surface properties.

30 The present invention further discloses a method for making such pellets for all the formulations of the invention. The manufacturing process can vary slightly for each product depending on the plasticizer loading. The current

process requires multiple passes through a co-rotating twin screw extruder with the product being pelletized at the end of each pass, and then refeed into the extruder for the further addition of plasticizer. The compositions with 90 percent plasticizer or more need three passes, while lower plasticizer loadings may require only two. It is important to note that the materials are pelletized with the pelletizing aid after both passes. The concentration of the pelletizing aid in the water can range from about 0.1 percent to about 3 percent by weight, preferably about 0.1 to about 1 percent by weight based on anticipated production rate for each pass. A specific preferred manufacturing process comprises:

- 10 a) blending the hot melt components to form a substantially homogeneous hot melt mixture;
- b) forcing said substantially homogeneous hot melt mixture through a die having a series of voids in a circular pattern to form a series of substantially homogeneous hot melt ribbons;
- 15 c) further forcing said homogeneous hot melt ribbons past rotating blades in substantially parallel position to said die, cutting said substantially homogeneous hot melt ribbons to form resultant pellets;
- d) substantially solidifying said pellets by use of a liquid cooling medium said liquid cooling medium containing a pelletizing aid, being circulated past said die and rotating blades on the side where said substantially homogeneous hot melt ribbons emerge;
- 20 e) transporting said hot melt pellets to a drying area;
- f) substantially removing liquid from said hot melt pellets by blowing.
- 25

As depicted above, the pelletizing aid is present in the cooling medium. It can also be added to the hot melt composition prior to blending or during the pelletizing steps by cofeeding a solution of pelletizing aid with the hot melt composition.

- 30 As noted above, it is well known in the art that stabilizers or antioxidants can also be added to the compositions in small amounts and have no effect on the other physical properties of the compositions. Other compounds that could be

added that also do not effect physical properties are pigments for color, fluorescing agents, and any compounds that mask odor. Additives such as these are known to one of skill in the art.

This invention is further illustrated by the following non-limiting
5 examples.

EXAMPLES

Test Methods

10 1. Melt Viscosities

The melt viscosities of the hot melt adhesives were determined on a Brookfield Thermosel Viscosmeter Model DV-II+. using either a number 21 or 27 spindle.

15 2. Specific Gravity

The specific gravity was determined using test method ASTM D792 with isopropyl alcohol as the liquid.

3. Mettler Softening Point

20 The Mettler softening points are determined using test method ASTM D3461.

4. Dynamic Temperature Steps

Storage modulus, G' , at 25°C and T_g were determined using a Rheometrics
25 Scientific Dynamic Mechanical Spectrometer Model # RDS7700. The parallel plates used had a 25 mm diameter and a 1.502 mm gap. The instrument was set to a frequency of 10 rads/sec and temperature sweep was performed from 180°C to -50°C.

30 5. Bloom Gelometer

Rigidity of the samples was determined using a Precision Bloom Gelometer Catalog No. 68705.

EXAMPLES 1-4

The following compositions are provided for illustrative purposes only.

These examples illustrate the physical properties achieved with these types
5 of hot melt compositions but there are many more compositions with differing
physical characteristics.

Examples 1 and 2 illustrate the invention using only a high molecular
weight block substantially linear A-B-A block copolymer. Examples 3 and 4
illustrate the use of a blend of a high molecular weight block copolymer and
10 another block copolymer. These examples illustrate compositions that are useful
for molded articles. The dynamic temperature steps are especially illustrative of
this. See exhibit no. 1.

TABLE I
Composition By Weight Percent

Example	1	2	3	4
Kraton G1651	10.0	5.0	7.0	7.0
Kraton G1650		5.0	12.0	17.0
Kaydol Oil	89.5	89.5	80.0	75.0
*Antioxidant	0.1	0.1	1.0	0.5
**UV Absorber	0.4	0.4		0.5
***Pigment		Minute Amount	Minute Amount	
About 0.1% Shamrock S-395 Pelletizing aid was added to each of the compositions.				
• Either Irganox 1076 antioxidant or Irganox 1010 antioxidant or a blend of the two may be used.				
** A blend of approximately half Tinuvin 770 and half Tinuvin 328 was used.				
***Minute amounts of either Sudan Blue 670, Sudan Orange 220, or Sudan Yellow 146 or blends thereof may be used.				

Table 2
Physical Characteristics

Example	1	2	3	4
Method Used				
Specific Gravity	ASTM D792	0.86	0.86	0.86
Density (#/gal)	ASTM D792	7.1	7.1	7.2
Viscosity @ 325°F		143.250 cp	1,770 cp	
Viscosity @ 350°F		21,625 cp	770 cp	
Viscosity @ 375°F		4,350 cp	190 cp	
Viscosity @ 400°F		1,060 cp	60 cp	
Mettler Soften Pt (°F)	ASTM D3461	282.8 ± 2.9	255.8 ± 0.3	
G' at 300°F	RDS-Parallel Plates	2.64E+04	3.29E+03	4.18E+04
G' at 200°F	Frequency=1 0 rad/s	4.76E+04	1.97E+04	2.11E+05
G' at 77°F	Initial Temp = 356°F	4.27E+04	3.12E+04	5.14E+05
Tg(upper)-°C(°F)	Initial Temp = 356°F		97.9(208.2)	104.9(220.8)
Tg(lower)-°C(°F)	Initial Temp = 356°F	-58.1(-72.6)	-54.3(-65.7)	-56.9(-70.4)

Examples 5 and 6 and Comparative Example A

Examples 5 and 6 illustrate compositions which may be used as hot melt pressure sensitive adhesives. Comparative example A is an example of a composition where G' falls outside the parameters specified for a hot melt pressure sensitive composition. From Table 4
5 it can be seen that it is necessary to raise the temperature to nearly 100°C for G' to fall within the pressure sensitive range.

Table 3
Composition By Weight Percent

	5	6	A
Kraton D4433-X (Linear SIS)	45.0		
Europrene Sol T190 (Linear SIS)		50.0	
Kraton D-1184 (Radial SBS)			50.0
Zonester 100	20.0		
Escorez 1310LC	35.0		
Wingtack Extra		50.0	
Zonatac 105			50.0
Antioxidant	0.2	0.2	0.2
About 0.1% Shamrock S-395 Pelletizing Aid was added to each of the Compositions.			
Antioxidant Irganox 1010, hindered phenolic antioxidant.			

Table 4

Rheology Data

G' @ (dynes/cm ²)	Example 5	Example 6	Comparative A
(77°F)25°C	9.0 x 10 ³	1.4 x 10 ⁶	8.3 x 10 ⁶
(100°F)38°C	6.5 x 10 ³	1.1 x 10 ⁶	6.9 x 10 ⁶
(200°F)93°C	3.0 x 10 ³	4.5 x 10 ³	2.7 x 10 ⁶
(300°F)149°C	1.1 x 10 ³		7.5 x 10 ³
T _g (°C)	8	4	-7.0

Claims:

- I. A polymeric composition in pellet form, comprising:
 - I. From about 97% by weight to about 99.9% by weight of a tacky hot melt composition, comprising:
 - a) from about 5% by weight to about 90% by weight of a thermoplastic polymer;
 - b) from about 0% by weight to about 65% by weight of a tackifying resin;
 - c) from about 0% to about 50% by weight of a plasticizer; and
 - d) up to about 2% by weight of an antioxidant; and
 - II. From about 0.1% by weight to about 3% by weight of a pelletizing aid, wherein the tacky hot melt composition comprises some minimum amount of tackifier, plasticizer or both, and is a pressure sensitive adhesive having a storage modulus, G' , at about 25°C, of less than about 5×10^6 dynes/cm², and each pellet has a substantially tack-free surface.
2. A polymeric composition in pellet form comprising:
 - I. From about 97% by weight to about 99.9% by weight of a tacky hot melt composition, comprising:
 - a) from about 2% by weight to about 20% by weight of a high molecular weight block copolymer having the general configuration A-B-A and a weight average molecular weight greater than about 200,000;
 - b) from about 20% by weight to about 98% by weight of a compatible plasticizer;
 - c) from about 0% to about 30% by weight of a compatible polymer; and
 - II. From about 0.1% by weight to about 3% by weight of a pelletizing aid, wherein the polymeric composition has a tack-free surface prior to melting the pellets, and after melting and resolidification.

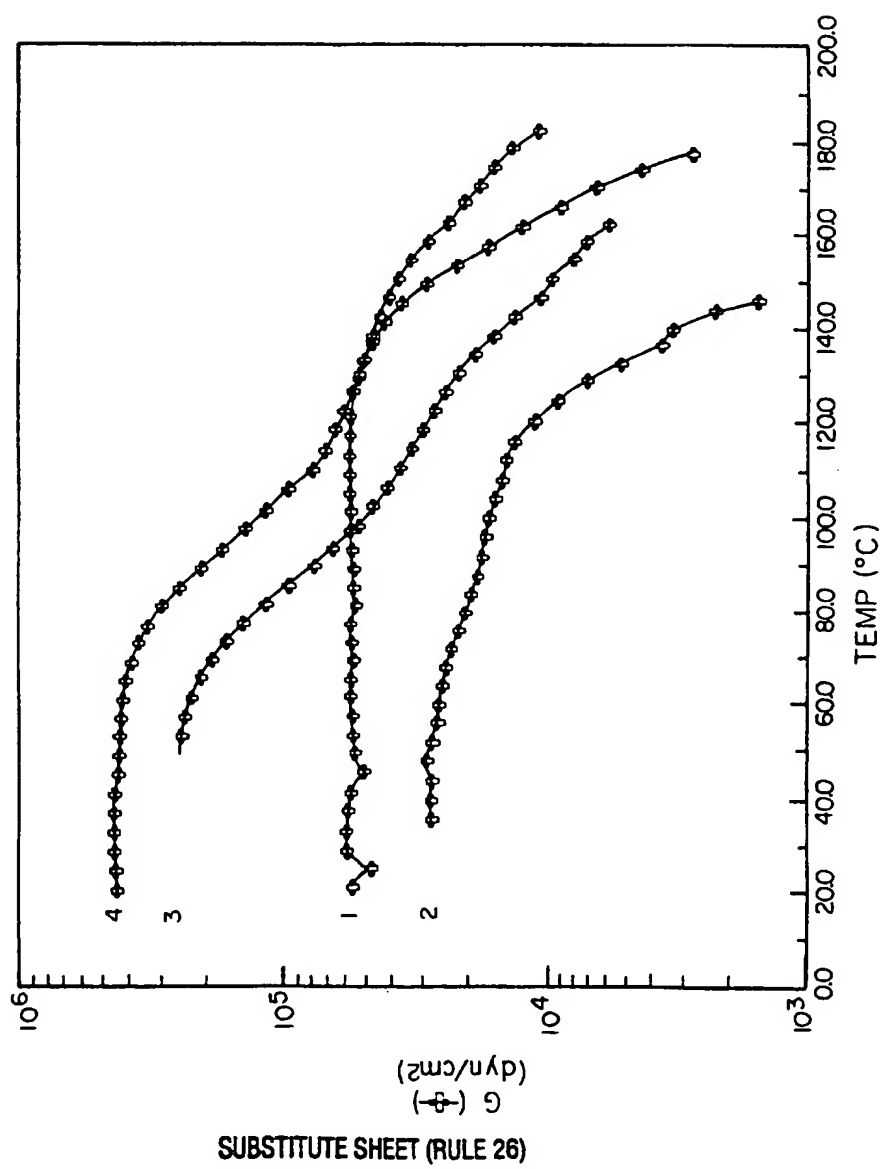
3. An article molded from a polymeric composition in pellet form wherein said polymeric composition in pellet form, comprises:
 - I. A tacky hot melt composition, comprising:
 - a) at least one high molecular weight triblock copolymer of the general configuration A-B-A; and
 - b) a plasticizer; and
 - II. A pelletizing aid,
wherein said pelletizing aid substantially surrounds the tacky composition such that the molded articles are soft, non-blocking and have a substantially tack-free surface.
4. A method for pelletizing the polymeric composition of any of Claims 1-2 comprising the steps of:
 - a) blending the hot melt components to form a substantially homogeneous mixture;
 - b) forcing said substantially homogeneous mixture through a die for forming substantially homogeneous ribbons and forming resultant pellets therefrom;
 - c) solidifying said pellets by use of a cooling medium; and
 - d) applying said pelletizing aid at some point during the pelletizing process.
5. A method for pelletizing the polymeric composition of any of Claims 1-2 comprising:
 - a) blending the hot melt components to form a substantially homogeneous mixture;
 - b) forcing said substantially homogeneous mixture through a die having a series of voids in a circular pattern to form a series of substantially homogeneous ribbons;
 - c) forcing said homogeneous ribbons past rotating blades in substantially parallel position to said die to form pellets;
 - d) substantially solidifying said pellets using a liquid cooling medium containing a pelletizing aid, said cooling medium being circulated past

said die and rotating blades on the side where said substantially homogeneous ribbons emerge;

- e) transporting said pellets to a drying area; and
 - f) substantially removing liquid from said pellets by blowing.
6. The polymeric composition of any of Claims 1-5 wherein said thermoplastic is a styrenic block copolymer having a styrene content from about 10% by weight to about 50% by weight and isoprene, butadiene, ethylene/butylene and ethylene/propylene midblocks and a diblock content of less than about 90%.
 7. The polymeric composition of any of Claims 1-5 wherein the thermoplastic polymer is selected from the group consisting of A-B-A triblock copolymer, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers, radial block copolymers, and grafted versions thereof; homopolymers, copolymers and terpolymers of ethylene; homopolymers, copolymers and terpolymers of propylene; and mixtures thereof.
 8. The polymeric composition of Claim 7 wherein said thermoplastic polymer is a homogeneous, substantially linear ethylene alpha olefin.
 9. The polymeric composition of any of Claims 1-5 wherein the tackifying resin is selected from the group consisting of aliphatic, cycloaliphatic and aromatic hydrocarbons and modified hydrocarbons and hydrogenated derivatives; terpenes and modified terpenes and hydrogenated derivatives; and rosins and modified rosins and hydrogenated derivatives; and mixtures thereof.
 10. The polymeric composition of any of Claims 1-5 wherein the plasticizer is selected from the group consisting of mineral based hydrocarbon oils, petroleum based hydrocarbon oils, polybutene, polyisobutylene, liquid tackifying resin, liquid elastomers, functionalized oils, fatty oils and mixtures thereof.
 11. The polymeric composition of any of Claims 1-5 wherein the pelletizing aid is selected from the group consisting of polyethylene waxes, modified polyethylene waxes, polyamide waxes and stearamide waxes and mixtures thereof.
 12. The polymeric composition of any of Claims 1-5 wherein the pelletizing aid is a polyethylene wax.

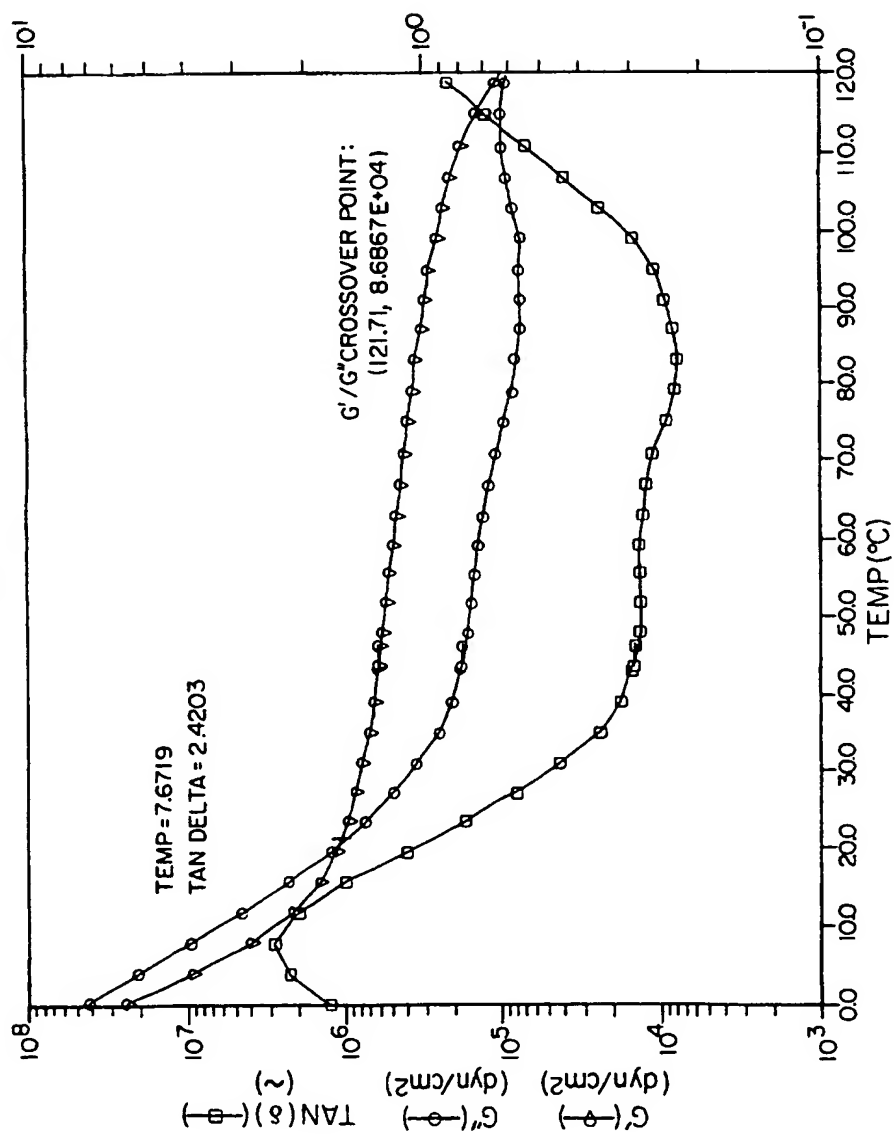
13. The polymeric composition of Claim 12 wherein the pelletizing aid is in powder form.
14. The method of any of Claims 4-5 wherein the blending step is carried out by means of a twin screw extruder.
15. The method of Claim 4 wherein the pelletizing aid is introduced in a manner selected from the group consisting of during the blending step, in the cooling medium and after solidification of the pellets and combinations thereof.
16. The polymeric composition of any of Claims 2-3 wherein the compatible polymer is selected from the group consisting of A-B-A triblock copolymers, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers, radial block copolymers and grafted versions thereof.
17. The polymeric composition of Claim 16 wherein the B block is selected from the group consisting of ethylene-propylene, ethylene-butylene and mixtures thereof.
18. The polymeric composition of Claim 17 wherein the A block is polystyrene.
19. The polymeric composition of any of claims 2-3 comprising a blend of between about 5% by weight and about 20% by weight of a high molecular weight block copolymer having the general configuration A-B-A, said block copolymer having polystyrene end blocks and a molecular weight greater than about 200,000; a compatible block copolymer of less than about 30% by weight; between about 50% by weight and about 95% by weight of a compatible plasticizer; and between about 0.01% by weight and about 0.6% by weight of a pelletizing aid comprising a polyethylene wax.
20. Molded article of Claim 3 wherein said article is selected from the group consisting of drum pads, shoe soles, therapeutic hand exercising grips, shock absorbers, acoustical insulators, pads for athletic gear, pads for medical equipment, furniture pads, bandages, burn victim bandages, synthetic skin and special effects articles.

Fig. 1



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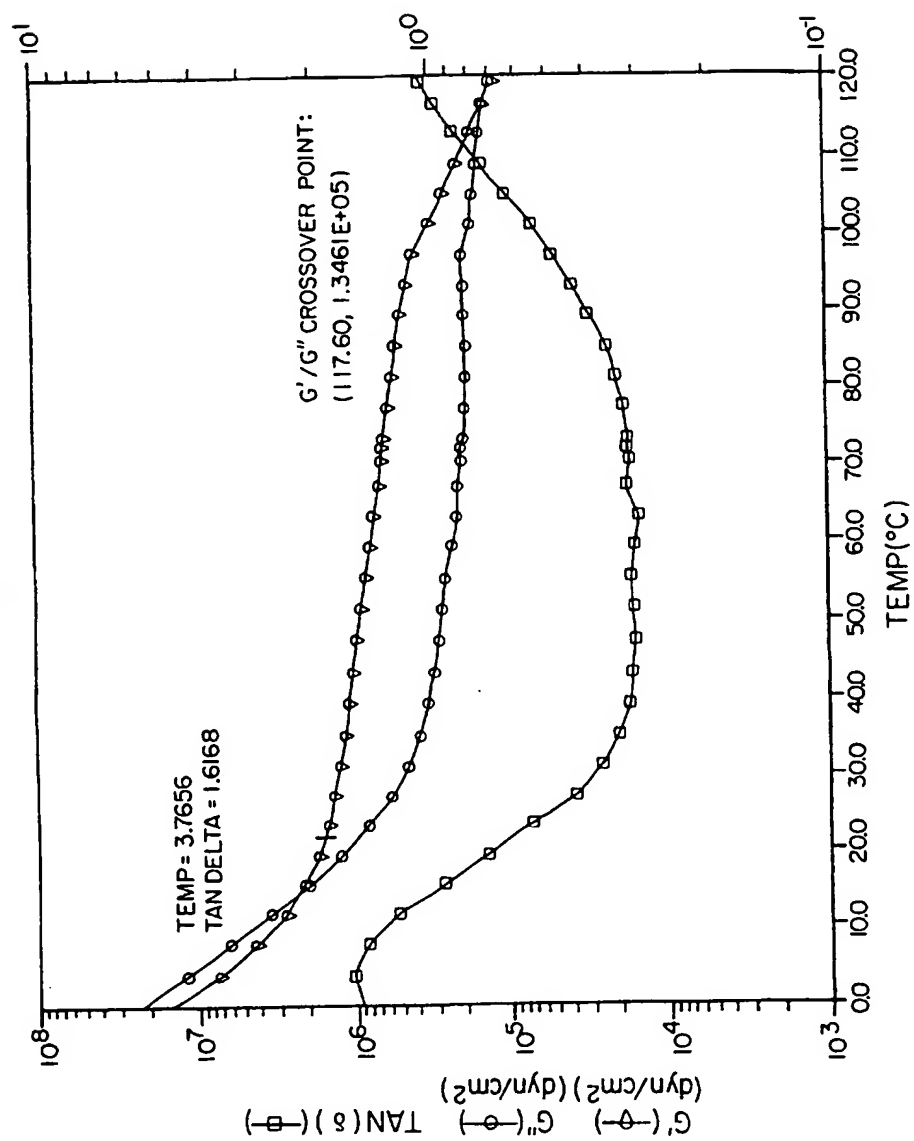
Fig. 2



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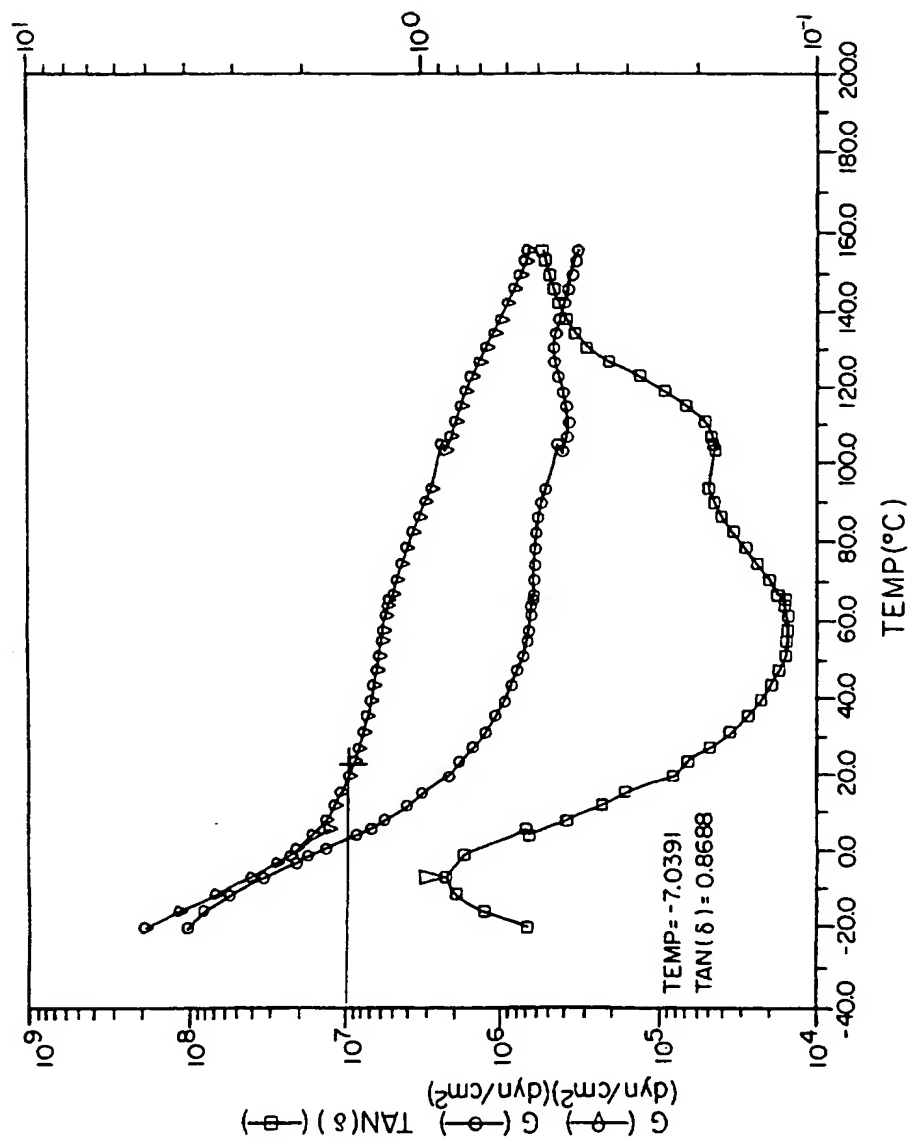
Fig. 3



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Fig. 4



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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08J 3/12, C09J 5/06	A3	(11) International Publication Number: WO 97/19582 (43) International Publication Date: 5 June 1997 (05.06.97)
(21) International Application Number: PCT/US96/18507 (22) International Filing Date: 18 November 1996 (18.11.96) (30) Priority Data: 08/559,006 16 November 1995 (16.11.95) US (71) Applicant: H.B. FULLER LICENSING & FINANCING, INC. [US/US]; 1200 Willow Lake Boulevard, St. Paul, MN 55110-5132 (US). (72) Inventors: SIMMONS, Eugene; 3440 Montmorency Street, Vadnais Heights, MN 55110 (US). SWEENEY, Kevin; 338 Wedgewood Drive, Mahtomedi, MN 55115 (US). LINDQUIST, Jeffrey; 9646 Indian Boulevard, Cottage Grove, MN 55016 (US). OLSON, Christopher; 5154 Parkside Drive, Paducah, KY 42001 (US). CARTES, Freddie; 1020 Wayside Drive, Paducah, KY 42003 (US). FARMER, James; 602 Newton, Johnston, IL 62951 (US). (74) Agents: STEINKRAUS, Walter, J. et al.; 1540 Kinnard Financial Center, 920 Second Avenue South, Minneapolis, MN 55402 (US).	(81) Designated States: AU, BR, CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 3 July 1997 (03.07.97)	
(54) Title: A POLYMERIC COMPOSITION IN PELLET FORM (57) Abstract A polymeric composition in pellet form comprising a tacky hot melt composition, comprising a) from about 5 % by weight to about 90 % by weight of a thermoplastic polymer, b) from about 10 % by weight to about 65 % by weight of a tackifying resin, c) up to about 50 % by weight of a plasticizer, d) up to about 2 % by weight of an antioxidant, and a pelletizing aid, wherein the tacky hot melt composition is a pressure sensitive adhesive having a storage modulus, G', at about 25 °C, of less than about 5 x 10 ⁶ dynes/cm ² , and each pellet has a substantially tack-free surface. This invention further discloses a polymeric composition in pellet form suitable for molding articles. The composition comprises a tacky hot melt composition comprising at least one high molecular weight triblock copolymer of the general configuration A-B-A and a plasticizer and a pelletizing aid. The pelletizing aid substantially surrounds the tacky composition such that the molded articles are substantially free from surface tack. A method of forming the pellets is also disclosed.		

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INTERNATIONAL SEARCH REPORT

International Application No

PC/US 96/18507

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J3/12 C09J5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 115 307 A (NATIONAL STARCH AND CHEMICAL CORPORATION) 8 August 1984 see claims 1-8 see page 4, line 24 - page 5, line 4 see page 6, line 2 - page 7, line 13 see page 7, line 16-25; figures 1,2 see page 8, line 1 - page 9, line 12 see examples I,III ---	1-13,15, 19,20
X	EP 0 410 914 A (EASTMAN KODAK COMPANY) 30 January 1991 see claims 1-3,5,6,11,14,15 see example 6 ---	1,4,5, 7-9, 11-13,15
X	US 3 779 785 A (C.J.STILES ET AL.) 18 December 1973 see claims 1,5 ---	1,4,7,8
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

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Hallemeesch, A

INTERNATIONAL SEARCH REPORT

International Application No.

PC1/US 96/18507

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 0 575 900 A (BASF AKTIENGESELLSCHAFT) 29 December 1993 see claims 1-5 ---	1,7,8
X	GB 2 142 255 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 16 January 1985 see claims 1-7 see page 1, line 38 - page 2, line 2 ---	1,6,7,9, 11
P,X	WO 96 00747 A (NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION) 11 January 1996 see claim 1 see page 3, line 15 - page 6, line 6 see example 1 ---> The figure mentioned at page 3, lines 10-14, was not available at the time of the international search -----	1,4,6-15

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International Application No.

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		NO 960712 A	22-02-96

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 23/08, 23/12, 51/06, E04F 15/10	A1	(11) International Publication Number: WO 97/10298 (43) International Publication Date: 20 March 1997 (20.03.97)
(21) International Application Number: PCT/SE96/01094 (22) International Filing Date: 4 September 1996 (04.09.96) (30) Priority Data: 9503197.7 15 September 1995 (15.09.95) SE (71) Applicant (for all designated States except US): TARKETT AB [SE/SE]; S-372 81 Ronneby (SE). (72) Inventor; and (75) Inventor/Applicant (for US only): LUNDQUIST, Eskil [SE/SE]; Bondevägen 6, S-372 33 Ronneby (SE). (74) Agent: AWAPATENT AB; P.O. Box 5117, S-200 71 Malmö (SE).	(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: FLOORING MATERIAL (57) Abstract <p>A flooring material comprises 30-70 parts by weight of a copolymer of ethylene and an α-olefin having 4-10 carbon atoms, preferably an ethylene/octene copolymer, 20-40 parts by weight of polypropylene, 5-20 parts by weight of a cross-linked ethylene polymer, preferably a copolymer of ethylene and an ethylenically unsaturated silane compound, 10-25 parts by weight of an organic filler, preferably polyethylene having a melt index below 0.1 g/10 min (190 °C/21.6 kg) and a phase stability in the flooring material of at least about 200 °C, 0.2-7 parts by weight of a flame retardant, preferably silicone and magnesium stearate, 0.1-2 parts by weight of an antistatic agent, and 0.1-1 part by weight of a stabiliser. The flooring material is free from inorganic fillers.</p>		

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FLOORING MATERIAL

The invention relates to a flooring material, and more specifically concerns a halogen-free flooring material that is free from inorganic fillers.

In order to be acceptable, a flooring material has
5 to possess a number of different properties, which are more or less incompatible. One such property is processibility, i.e. it has to be possible to process the material so as to form it into a sheetlike or weblike flooring material. In this context, it is of primary importance that the material is easily calendered. Further-
10 more, the flooring material should be wear- and scratch-resistant, and its surface should exhibit such friction as to be suited for use, for instance by people walking on it. In addition, the material should be weldable,
15 enabling the provision of tight joints when putting down a floor. The flooring material should, moreover, enable optimum cleaning, and should thus be polishable and preferably have a dirt-repellent surface. The resilience and the softness of the flooring material, which are measured
20 by indentation-recovery, are essential qualities, which are of importance in order to avoid lasting indentations of furniture and rolling objects, such as office chairs, and which also affect the walking comfort. Moreover, the fire resistance is vital, and the flooring material
25 should be as fire-resistant as possible while, if catching fire, giving off as little irritant smoke as possible.

Using polyvinyl-chloride-based materials, such as polyvinyl chloride (PVC) and vinyl chloride copolymers,
30 primarily copolymers of vinyl chloride and vinyl acetate, as flooring materials is previously known. These materials have many advantages, such as fetching a low price, being easy to process, and having a great range of variation, i.e. the properties of the material are easily

adjusted with the aid of various additives, such as plasticisers and pigments.

However, PVC-based flooring materials also suffer from a number of drawbacks. In recent years, attention has focused on these drawbacks, and efforts have been made to provide other synthetic flooring materials not based on PVC. Among other things, PVC-based flooring materials are disadvantageous in that they contain chlorine (halogen), which forms hydrogen chloride upon combustion. Also, the various additives included in PVC-based flooring materials and typically containing different metal compounds yield metal-containing residues when combusted. For reasons of costs and properties, PVC-based flooring materials further contain considerable amounts of fillers which generally are of inorganic type, such as calcium carbonate, clays, and aluminium trihydrate. These inorganic fillers are non-combustible and thus leave a contaminating residue, which has to be deposited, when the flooring material is combusted. When PVC-based flooring materials are combusted, various additives, such as lime or dolomite, are used for binding released chlorine. As a result, larger amounts of material have to be deposited, and the costs are increased.

Also, an addition of inorganic fillers has an adverse effect on the wear resistance of the material.

In an effort to obviate the above-mentioned drawbacks of the PVC-based flooring materials, one has, in recent years, tried to develop halogen-free flooring materials, which usually are based on different mixtures of olefin polymers. US Patent 5,276,082 teaches such a halogen-free flooring material, which comprises a mixture of a silane-grafted polymer and an ungrafted polymer. To be more specific, the mixture contains a first component, which is a copolymer of ethylene and another monomer selected from the vinyl esters of saturated and unsaturated carboxylic acids, preferably vinyl acetate, and a second component, which consists of a silane-grafted ver-

sion of the above-mentioned ethylene copolymer, i.e. preferably silane-grafted ethylene/vinyl acetate. A third essential component of the mixture is a filler, preferably calcium carbonate, clay or aluminium trihydrate,
5 which is present in an amount of 30-90% by weight.

Even though the flooring material according to US Patent 5,276,082 is free from halogen, it has, like other prior-art flooring materials, a high content of inorganic fillers, which result in the formation of environmentally
10 questionable or objectionable metal-containing substances and ash when destroyed by combustion of the flooring material.

This invention aims at obviating the drawbacks of the prior art by providing a halogen-free flooring material which is not based on PVC and, in addition, is free
15 from inorganic fillers.

According to the invention, this aim is achieved by a flooring material comprising a defined composition of olefin polymers in combination with an organic filler and
20 certain additives.

To be more specific, the invention provides a flooring material which is characterised in that it comprises 30-70 parts by weight of a copolymer of ethylene and an
25 α -olefin having 4-10 carbon atoms,
20-40 parts by weight of polypropylene,
5-20 parts by weight of a crosslinked ethylene polymer,
10-25 parts by weight of an organic filler,
0.2-7 parts by weight of a flame retardant,
0.1-2 parts by weight of an antistatic agent, and
30 0.1-1 part by weight of a stabiliser,
and that the material is free from inorganic fillers.

Preferably, the flooring material according to the invention comprises
40-60 parts by weight of a copolymer of ethylene and an
35 α -olefin having 4-10 carbon atoms,
25-30 parts by weight of polypropylene,
5-15 parts by weight of a crosslinked ethylene polymer,

10-20 parts by weight of an organic filler,
0.6-4 parts by weight of a flame retardant,
0.1-1 part by weight of an antistatic agent, and
0.1-1 part by weight of a stabiliser.

5 These and other distinctive features and advantages of the invention will appear in more detail from the following description as well as the appended claims.

As indicated above, the flooring material according to the invention contains a first component in the form
10 of 30-70 parts by weight, preferably 40-60 parts by weight, of a copolymer of ethylene and an α -olefin having 4-10 carbon atoms. This component is intended to impart elasticity to the material and to reduce its melting temperature, resulting in a wider temperature range for
15 processing and hence improving the processibility of the material. The copolymer also improves the properties of the flooring material as regards wear resistance and indentation-recovery. In order to attain an aimed-at processing range of about 150-200°C, the melting point of
20 the copolymer should be below 120°C, preferably ranging between about 50°C and 100°C. The density of the copolymer is about 0.87-0.92 g/cm³. Octene is a preferred α -olefin comonomer, and an instance of a preferred copolymer is the ethylene/octene copolymer available from Dow
25 under the designation DSH 8501.00.

As a second component, the flooring material according to the invention contains 20-40 parts by weight of polypropylene, preferably 25-30 parts by weight. This component enhances the hardness of the material and
30 reduces its friction. In addition, the dirt-repellent qualities of the material are improved, i.e. the flooring material becomes easier to clean. An example of a preferred propylene polymer is the one available from Borealis AB under the tradename of Embryon[®] HG 770 J
35 having a density of 0.903 g/cm³ and a melt flow of 25 g/10 min (230°C/2.16 kg).

As a third component, the flooring material according to the invention contains 5-20 parts by weight, preferably 5-15 parts by weight, of a crosslinked ethylene polymer, preferably a silane-crosslinked ethylene polymer. The preferred silane-crosslinked ethylene polymer may consist of either a graft copolymer of ethylene and an ethylenically unsaturated, hydrolysable silane compound or, which is preferred, a copolymer of ethylene and an ethylenically unsaturated, hydrolysable silane compound. As silane compound, use may, for instance, be made of vinyl silanes, such as vinyl trimethoxy silane. Such silane (graft) copolymers are crosslinked under the action of water and a silanol condensation catalyst, such as dibutyltin dilaurate. The crosslinked ethylene polymer component improves the processing properties of the mixture by increasing the viscosity of the material and hence reducing the mobility therein, thereby facilitating the achievement of the aimed-at patterns. Furthermore, the crosslinked ethylene polymer improves the properties of the material as regards wear and indentation-recovery. In order to optimise the effect of the crosslinked ethylene polymer component in the composition, the degree of crosslinking should not be too high. Preferably, the silane compound constitutes about 1-30% by weight, preferably about 1-15% by weight, of the crosslinked ethylene polymer. As an example of a preferred crosslinkable ethylene polymer, mention may be made of the products LE 4421 and LE 4438 available from Borealis AB. The former is the polymer itself, whereas the latter is the crosslinking catalyst.

As a fourth component, the flooring material according to the invention contains 10-25 parts by weight, preferably 10-20 parts by weight, of an organic filler. By the term "organic filler" is meant an organic material which, upon combustion, leaves a residue of no more than 10% by weight, preferably no more than 5% by weight, and which preferably consists chiefly, i.e. to at least 95%

by weight, of carbon, hydrogen and oxygen. According to the invention, this organic filler is intended to replace, either by itself or in combination with the other components, the inorganic fillers generally used in prior-art flooring materials. In order to be able to perform its function properly, the organic filler should be phase-stable, i.e. form a phase of its own in the form of discrete particles in the flooring material, when the flooring material is being processed. Since the flooring material is normally processed at a temperature below about 200°C, this means that the organic filler should be phase-stable or "particle-stable", i.e. be present in the form of discrete particles in the flooring material, up to a temperature of at least about 200°C. According to the invention, the organic filler preferably is a polymer material selected from one or more of: starch, cellulose and polyethylene, the polyethylene having a melt index below 0.1 g/10 min (190°C/21.6 kg) and a phase stability to at least about 200°C. When used as fillers, starch and cellulose are advantageous in that they both have fairly high contents of hydroxyl groups, which are cross-linked with the silane groups of the crosslinkable ethylene polymer component. This provides yet another possibility of adjusting the properties of the material. As an example of a preferred polyethylene filler, mention may be made of the polymer marketed under the tradename of Lupolen UHM 201 by BASF and having a density of 0.93 g/cm³ and a melt flow below 0.1 g/10 min (190°C/21.6 kg). This polyethylene filler also contributes to giving the flooring material a harder surface.

Apart from the components mentioned above, the flooring material according to the invention contains certain additives, as appears from the foregoing and will be described in more detail below.

In order to obtain the aimed-at flame resistance, the material contains 0.2-7 parts by weight of a flame retardant, preferably 0.6-4 parts by weight. Even though

conventional flame retardants are not excluded from the flooring material according to the invention, it is especially preferred that the flame retardant is a silicone replacing conventional antimony- or halogen-containing flame retardants. The effect of the silicone is enhanced by combining it with an organic metal salt, more specifically an organic salt of a metal from the group IIA of the Periodic table. Preferably, the organic metal salt is magnesium stearate. The above flame retardant contents include both the silicone and the organic metal salt. Normally, the silicone is present in an amount of 0.1-5 parts by weight, preferably 0.5-3 parts by weight, while the organic metal salt is present in an amount of 0.1-2 parts by weight, preferably 0.1-1 part by weight. In addition to imparting the aimed-at flame-retardant properties to the material, the flame retardant has a lubricating ability, which facilitates the processing of the material and further enhances its impact resistance. As an instance of a preferred flame retardant, mention may be made of the product available under the tradename of SFR 100 Silicone Fluid from General Electric. Further details of this flame retardant are found in US Patent 4,387,176.

Moreover, the flooring material according to the invention contains 0.1-2 parts by weight of an antistatic agent, preferably 0.1-1 part by weight. This is an additive required in order to avoid static charging of the flooring material and to improve the dirt-repellent properties of the finished material. The antistatic agent employed in the flooring material according to the invention can be selected from known antistatic agents, but preferably consists of glycerol stearate, for instance in the form of the product available from Hoechst under the tradename of Hostastat FE-2.

Finally, the flooring material contains a stabiliser, which has a stabilising effect as regards oxidation and decomposition (yellowing), which otherwise may

occur, for instance in the presence of the antistatic agent mentioned above. As an example of a suitable stabiliser, mention may be made of sterically hindered phenols, for instance those available from Ciba under the tradename of Irganox 1010.

Apart from the components indicated above, the flooring material according to the invention may contain optional conventional additives and pigments.

With the composition described above, in particular the lack of inorganic fillers, the flooring material according to the invention have only marginal contents of metals that are questionable or objectionable from the point of view of the environment and are released by leaching, biological-chemical decomposition or combustion, i.e. the content of such metals as aluminium, lead, cadmium, copper, chromium and zinc is basically zero.

The inventive flooring material of the above composition can be produced by using conventional techniques and conventional equipment. There should thus be no need of any detailed description of the production of the flooring material according to the invention. As an example of such production, it may, however, be mentioned that the components and the additives may first be weighed and mixed in cold state, whereupon the resulting mixture is melted and extruded in the form of bands, which are fed to a rolling mill and there are processed to webs. The resulting webs are cut to pieces or crushed and may then immediately be rolled or pressed to form the finished flooring material. Alternatively, the cut or crushed webs may first be stored and then at a suitable moment be heated and rolled or pressed to form the finished flooring material.

The invention will now be further elucidated with the aid of a few non-restricting Examples. The following comparison is based on two apparently equivalent, 2-mm-thick homogeneous flooring materials intended for public use. The one flooring material is produced in accordance

with the invention, while the other flooring material is a PVC-based flooring material of known composition.

The upper side and the lower side of the flooring material according to the invention and the upper side
5 of the PVC-based flooring material were subjected to a corona treatment in order to increase the adhesion. Then, the upper side and the lower side of the flooring material according to the invention were coated with 5 g
(based on dry solids) of a primer (based on RIC from PPG
10 Industries) per m². Finally, the one surface (the upper side) of the two flooring materials was coated with 10 g
(based on dry solids) of polyurethane (based on NeoRez R-986 from Zeneca Resins) per m². The purpose of this polyurethane layer is to make the flooring materials easier
15 to clean and enhance their dirt-repellent capacity. Since the polyurethane layer affects the wear resistance, the wear-resistance test in Example 1 was also performed on flooring materials having no such surface layer of polyurethane. The other properties of the flooring material
20 are only marginally affected by the polyurethane layer.

The two flooring materials have the following composition.

Flooring Material According to the Invention

<u>Parts by weight</u>	<u>Tradename</u>	<u>Designation</u>	<u>Supplier</u>
47.7	DSH 8501.00	Ethylene- α -olefin copolymerisate	DOW Chemicals
26	Embryon [®] HG770J	Polypropylene	Borealis
8.7	LE 4421	Crosslinkable ethylene polymer	Borealis
0.4	LE 4438	Catalyst	Borealis
13	Lupolen UHM201	UHMW - PE	BASF
1	SFR100	Flame retardant	General Electric
0.7	Parma	Magnesium stearate	Bärlocher
0.5	Hostastat FE-2	Antistatic agent	Hoechst
0.1	Irganox 1010	Stabiliser	Ciba
1.9		Pigment	

PVC-based Flooring Material (Tarkett Eminent from
Tarkett AB

<u>Parts by weight</u>	<u>Tradename</u>	<u>Designation</u>	<u>Supplier</u>
47.1	Norvinyl S6260	PVC	Norsk Hydro Plast AB
17.2	DEHP	Diethylhexyl phthalate	Neste Chemicals
0.7	Lankromark LZ 1694	BaZn Stabiliser	Akcros Chemicals
0.9	Lankroflex EWS	Epoxidised soy- bean oil	Akcros Chemicals
0.3	Tefacid 1 VT65	Stearic acid	Tefac AB
12.6	Strådolomit A30	Dolomite	Stråbruken AB
10.8	Sjöhästen FF	Calcium carbonate	Malmökrita AB
8.4	Kaolin FA	Kaolin	Zavod
2		Pigment	

Example 1

In this Example, the wear resistance of the flooring material according to the invention was compared with that of the prior-art, PVC-based flooring material. The wear resistance was determined according to the standard EN 660.

In the test, the wear resistance of the flooring material according to the invention was found to be 1.4 mm³/100 turns for material having a surface layer of polyurethane and 0.65 mm³/100 turns for material having no such surface layer, whereas the PVC-based flooring material had a wear resistance of 3.38 mm³/100 turns when provided with a surface layer of polyurethane and a wear resistance of 3.06 mm³/100 turns when not provided with such a surface layer. Thus, the flooring material according to the invention had a much better wear resistance than the known PVC-based flooring material.

Example 2

In this Example, the fire propagation and the smoke emission of the flooring material according to the invention and of the prior-art PVC-based flooring material were tested. The test was carried out in accordance with the standard SIS 024825. According to this standard, the fire propagation should be below 55 cm, and the fire emission should be below 30%.

In the test, the flooring material according to the invention was found to have a fire propagation of 40 cm and a smoke emission of 3%, whereas the PVC-based flooring material was found to have a fire propagation of 22 cm and a smoke emission of 16%. Both materials thus had a fire propagation well below the standard limit. However, the flooring material according to the invention gave off very little smoke and much less than the PVC-based flooring material.

In addition to this test, the fire propagation and the smoke emission were tested according to the so-called Radiation Panel Test. According to this test, an accept-

ed material should require a power exceeding 0.45 W/cm^2 for fire propagation, and the material should exhibit a smoke emission below $750\% \cdot \text{min}$.

In this test, the flooring material according to the invention required 0.50 W/cm^2 in order to catch fire and had a smoke emission of $55\% \cdot \text{min}$, whereas the PVC-based flooring material required 0.99 W/cm^2 in order to catch fire and had a smoke emission of $300\% \cdot \text{min}$. Also in this case, both materials had fire-propagation values and smoke-emission values below the standard limit. However, the flooring material according to the invention gave off much less smoke than the PVC-based flooring material.

Example 3

In this Example, the indentation-recovery of the flooring material according to the invention and the PVC-based flooring material were determined in accordance with the standard SIS 923505.

In this test, the flooring material according to the invention had an indentation of 0.88 mm after 5 min and a recovery of 89.8% after 24 h . The corresponding values of the PVC-based flooring material were, respectively, 0.74 mm and 87.8% . Thus, the flooring material according to the invention had a slightly higher indentation value than did the PVC-based flooring material, but this was compensated for by a higher degree of recovery.

Example 4

In this Example, one determined the residues left after combustion of the flooring material according to the invention and the PVC-based flooring material, as well as the deposition requirement created by these combustion residues. The flooring materials were burnt to ashes at 550°C .

The results of the test are indicated in the Table below.

Flooring material	<u>Ashes after combustion</u>		<u>Deposition requirement for ashes and bound chlorine</u>	
	kg/m ²	% by weight of starting material	kg/m ²	% by weight of starting material
Invention	0.12	5.9	0.12	5.9
PVC	0.84	27.6	2.4	70

It is evident from this Table that the flooring material according to the invention yields less ash and thus involves much smaller deposition requirements than does the PVC-based flooring material. The much greater deposition requirement of the PVC-based flooring material is, inter alia, due to the addition of lime/dolomite to bind released chlorine.

10 Example 5

This Example aims at demonstrating the content of metals, which are environmentally objectionable and originate from fillers and other additives, found in the flooring material according to the invention and the PVC-based flooring material. Thus, the contents of these metals were determined in ashes from the combustion of the flooring materials by dissolving the ashes in concentrated nitric acid. The dissolution was performed by mixing the ashes and the nitric acid in a container of Teflon[®], whereupon the container was sealed and heated in a microwave oven. Samples that had not been burnt to ashes were used for determining the contents of cadmium and lead. The final determination of the metal contents was performed with the aid of Plasma emission spectrometry (ICP-AES) or Plasma mass spectrometry (ICP-MS). The metal contents determined appear from the Table below.

	Invention g/m ²	PVC g/m ²	Test method
Aluminium	0.002	12	ICP-AES
Lead	0.000	0.015	ICP-MS
Cadmium	0.0000	0.0001	ICP-MS
Copper	0.000	0.003	ICP-AES
Chromium	0.000	0.008	ICP-AES
Zinc	0.00	0.15	ICP-AES

It is evident from the Table that the flooring material according to the invention causes no, or but insignificant, environmental pollution owing to its metal content. It should be pointed out that the PVC-based flooring material has an adverse effect on the environment not only as a result of its metal content but also as a result of the addition of lime/dolomite to bind released chlorine.

CLAIMS

1. A flooring material, characterised in
5 that it comprises
30-70 parts by weight of a copolymer of ethylene and an
 α -olefin having 4-10 carbon atoms,
20-40 parts by weight of polypropylene,
 5-20 parts by weight of a crosslinked ethylene polymer,
10 10-25 parts by weight of an organic filler,
 0.2-7 parts by weight of a flame retardant,
 0.1-2 parts by weight of an antistatic agent, and
 0.1-1 part by weight of a stabiliser,
and that the material is free from inorganic fillers.
- 15 2. A flooring material as set forth in claim 1,
characterised in that it comprises
40-60 parts by weight of a copolymer of ethylene and an
 α -olefin having 4-10 carbon atoms,
25-30 parts by weight of polypropylene,
20 5-15 parts by weight of a crosslinked ethylene polymer,
10-20 parts by weight of an organic filler,
 0.6-4 parts by weight of a flame retardant,
 0.1-1 part by weight of an antistatic agent, and
 0.1-1 part by weight of a stabiliser.
- 25 3. A flooring material as set forth in claim 1 or 2,
characterised in that the α -olefin employed is
octene.
4. A flooring material as set forth in any one of
claims 1-3, characterised in that the cross-
30 linked ethylene polymer is a copolymer of ethylene and an
ethylenically unsaturated silane compound.
5. A flooring material as set forth in claim 4,
characterised in that the copolymer contains
1-30% by weight of the silane compound.
- 35 6. A flooring material as set forth in any one of
claims 1-5, characterised in that the organic
filler is selected from one or more of: starch, cellulose

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and polyethylene having a melt index below 0.1 g/10 min (190°C/21.6 kg) and a phase stability in the flooring material of at least about 200°C.

5 7. A flooring material as set forth in any one of claims 1-6, characterised in that the flame retardant comprises a silicone and a an organic metal salt.

8. A flooring material as set forth in claim 7, characterised in that the organic metal salt
10 is magnesium stearate.

9. A flooring material as set forth in any one of claims 1-8, characterised in that the anti-static agent comprises glycerol stearate.

10. A flooring material as set forth in any one of
15 claims 1-9, characterised in that the stabiliser is a sterically hindered phenol.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 96/01094

A. CLASSIFICATION OF SUBJECT MATTER		
IPC6: C08L 23/08, C08L 23/12, C08L 51/06, E04F 15/10 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: C08L, E04F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPODOC, CAPLUS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5276082 A (JOHN S. FORRY ET AL), 4 January 1994 (04.01.94), abstract, column 1, lines 8-12, column 2, lines 27-33 --	1-10
A	EP 0321760 A1 (HÜLS TROISDORF AKTIENGESELLSCHAFT), 28 June 1989 (28.06.89), abstract, page 2, lines 7-11 --	1-10
P,A	EP 0683205 A1 (ELF ATOCHEM S.A.), 22 November 1995 (22.11.95), abstract -- -----	1-10
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
17 December 1996		09 -01- 1997.
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer Agneta Österman Wallin Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/10/96

International application No.

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US-A- 5276082	04/01/94	CA-A- 2112529 DE-A- 4400035 GB-A- 2285258 GB-D- 9326571	30/06/95 06/07/95 05/07/95 00/00/00
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